

Recent Advances in Thermoplastic Puncture-Healing Polymers

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Abstract

Self-healing materials provide a route for enhanced damage tolerance in materials for aerospace applications. In particular, puncture-healing upon impact has the potential to mitigate significant damage caused by high velocity micrometeoroid impacts. This type of material also has the potential to improve damage tolerance in load bearing structures to enhance vehicle health and aircraft durability. The materials being studied are those capable of instantaneous puncture healing, providing a mechanism for mechanical property retention in lightweight structures. These systems have demonstrated healing capability following penetration of fast moving projectiles -- velocities that range from 9 mm bullets shot from a gun (~330 m/sec) to close to micrometeoroid debris velocities of 4800 m/sec. In this presentation, we report on a suite of polymeric materials possessing this characteristic.

Figure 1 illustrates the puncture healing concept. Puncture healing in these materials is dependent upon how the combination of a polymer's viscoelastic properties responds to the energy input resulting from the puncture event. Projectile penetration increases the temperature in the vicinity of the impact. Self-healing behavior occurs following puncture, whereby energy must be transferred to the material during impact both elastically and inelastically, thus establishing two requirements for puncture healing to occur: a.) The need for the puncture event to produce a local melt state in the polymer material and b.) The molten material has to have sufficient melt elasticity to snap back and close the hole.^{1,2} Previous ballistic testing studies revealed that Surlyn materials warmed up to a temperature ~98°C during projectile puncture (3°C higher than it's melting temperature).^{1,2} The temperature increase produces a localized flow state and the melt elasticity to snap back thus sealing the hole.

Table 1 lists the commercially polymers studied here, together with their physical properties. The polymers were selected based on chemical structure, tensile strengths, tensile moduli, glass transition temperature, melting temperatures, and impact strength. The thermal properties of the polymers were characterized by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Mechanical properties were assessed by a Sintech 2W instron according to ASTM D1708 or D638 at crosshead speeds of 5.08 cm/min.

7.6 cm x 7.6 cm panels of the different materials were prepared and ballistic testing was performed at various temperatures. The panels were shot with a .223 caliber semiautomatic rifle from a distance of 23 meters at various temperatures. Chronographs were used to measure initial and final bullet velocity. Temperatures at the site of impact were measured using a FLIR ThermoCAM S60 thermal camera. A Vision Research model Phantom 9 high speed video camera was used to capture high speed video footage of ballistics testing.

Surlyn and Affinity EG8200, both poly(ethylene) based copolymers, self-healed upon ballistic testing at ambient temperature (~24°C). Lexan, poly(butylene terephthalate) (PBT), and poly(butylene terephthalate)-co-poly(alkylene glycol terephthalate) (PBT-co-PAGT) polymers did not display self-healing upon ballistics testing when shot at approximately 25°C. However, these polymers displayed an improvement in damage tolerance upon ballistics testing at elevated temperatures (> 100°C). Poly(butadiene)-graft-poly(methyl acrylate-co-acrylonitrile) (PB-g-PMA-co-PAN) also displayed much improved healing when tested at 50°C and 100°C.

In summary, some commercially available polymers possessing instantaneous puncture self-healing functionality have been identified.

References

1. Kalista, S., M.S. thesis entitled, "*Self-healing Thermoplastic Poly(Ethylene-co-Methacrylic Acid) Copolymers Following Projectile Puncture*" submitted to the faculty of Virginia Polytechnic Institute and State University, Blacksburg, VA 2003.
2. Fall, R., M.S. thesis entitled, "*Puncture reversal of ethylene ionomers – Mechanistic Studies*" submitted to the faculty of Virginia Polytechnic Institute and State University, Blacksburg, VA 2001.
3. Klein, D, Cano, B.; Siochi, M., "*Development and ballistic testing of self-healing polymers.*" Not yet published, NASA-LARC 2005.

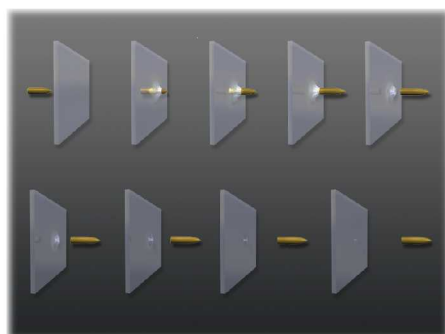


Figure 1: Bullet Penetration Schematic Diagram

Table 1: Physical Properties of Polymers

| Polymer | Tg (°C) | Tm (°C) | Test Temp (°C) | Elongation (%) | Tensile Strength (MPa) | Tensile Modulus (MPa) |
|-----------------|---------|----------|----------------|----------------|------------------------|-----------------------|
| Surlyn | -100 | 54,95 | 25 | 309 | 27.2 | 308.5 |
| Affinity | -68 | 39,53,75 | 25 | 947 | 9.3 | 5.9 |
| PB-g-PMA-co-PAN | 85 | - | 25,50,100 | 4.0 | 65.5 | 3300 |
| Lexan | 150 | - | 25, 100 | 2.0 | 59.0 | 2900 |
| PBT | 70 | 210 | 25, 100 | 250 | 50 | 2000 |
| PBT-co-PAGT | 66 | 180 | 28 | 500 | 6.9 | 188 |